

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF: :
SATOSHI NIIYAMA, ET AL : GROUP ART UNIT: 1756
SERIAL NO.: 09/807,425 :
FILED: July 3, 2001 : EXAMINER: SADULA, J.
FOR: LIQUID CRYSTAL OPTICAL
ELEMENT AND METHOD FOR
ITS PRODUCTION :

DECLARATION

COMMISSIONER FOR PATENTS

ALEXANDRIA, VIRGINIA 22313

SIR:

Now comes MASAYUKI KUWANO who deposes and says:

That my name is MASAYUKI KUWANO ;

That my address is 5-24-310, 3-chome, Nakamachi,

Musashino-shi, Tokyo, Japan;

That I know well both the English and Japanese languages;

That the attached English language translation is true and
correct translation of Japanese Patent Application No JP10/298624 filed on
October 20, 1998 to the best of my knowledge and belief.

I hereby declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

FURTHER DEPONENT SAITH NOT.

October 3, 2003
Date

Masayuki Kuwano
MASAYUKI KUWANO

AB-126-PCT
(F99-95)
3/3

Date of Application: October 20, 1998

Application Number: Patent Application JP10/298624

Applicant: Asahi Glass Company, Limited

【Type of Document】 PETITION FOR PATENT APPLICATION
【Reference No.】 980655
【Filing Date】 October 20, 1998
【Addressee】 Commissioner, Patent Office
【International Patent Classification】 G02F 1/13
G09K 19/02

【Title of the Invention】

LIQUID CRYSTAL OPTICAL ELEMENT AND METHOD FOR ITS
PRODUCTION

【Number of Inventions Stated in Claim(s)】 9

【Inventor(s)】

【Name】 Satoshi Niiyama

【Address or Residence】 Asahi Glass Company, Limited
1150, Hazawa-cho, Kanagawa-ku,
Yokohama-shi, Kanagawa

【Name】 Shinya Tahara

【Address or Residence】 Asahi Glass Company, Limited
1150, Hazawa-cho, Kanagawa-ku,
Yokohama-shi, Kanagawa

【Patent Applicant(s)】

【Identification No.】 000000044

【Name or Company Name】 Asahi Glass Company, Limited

【Representative(s)】

【Identification No.】 100090918

【Patent Attorney】

【Name or Company Name】 Kenji Senmyo

【Telephone Number】 03-3218-5647

【Identification of Fees】

【Prepayment account No.】 009830

[Amount of Payment]	21,000	
[List of Submitted Items]		
[Name of item]	Specification	1
[Name of item]	Abstract	1
[Burden of Proof]	Yes	

【TYPE OF DOCUMENT】 SPECIFICATION

【TITLE OF THE INVENTION】

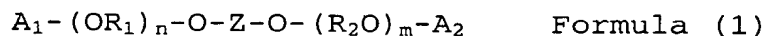
LIQUID CRYSTAL OPTICAL ELEMENT AND METHOD FOR ITS
PRODUCTION

5 【SCOPE OF THE CLAIM(S)】

【Claim 1】

A method for producing a liquid crystal optical
element, which comprises sandwiching a mixture of a
liquid crystal with an uncured curable compound between a
10 pair of substrates which are provided with transparent
electrodes and of which at least one is transparent, and
curing the curable compound to form a liquid
crystal/cured composite layer, wherein the curable
compound contains a compound of the formula (1):

15 【Ka 1】



wherein each of A_1 and A_2 which are independent of each
other, is an acryloyl group, a methacryloyl group, a
glycidyl group or an allyl group; each of R_1 and R_2 which
20 are independent of each other, is a C_{2-6} alkylene group; Z
is a bivalent mesogen structure; and each of n and m
which are independent of each other, is an integer of
from 1 to 10.

【Claim 2】

25 The method for producing a liquid crystal optical

element according to Claim 1, wherein Z is a 4,4'-biphenylene group, or a 4,4'-biphenylene group having part or all of hydrogen substituted by C₁₋₂ alkyl or halogen atoms.

5 **【Claim 3】**

The method for producing a liquid crystal optical element according to Claim 1 or 2, wherein each of R₁ and R₂ which are independent of each other, is an ethylene group or a propylene group.

10 **【Claim 4】**

The method for producing a liquid crystal optical element according to Claim 1, 2 or 3, wherein each of A₁ and A₂ which are independent of each other, is an acryloyl group or a methacryloyl group.

15 **【Claim 5】**

The method for producing a liquid crystal optical element according to Claim 1, 2, 3 or 4, wherein each of n and m which are independent of each other, is from 1 to 4.

20 **【Claim 6】**

The method for producing a liquid crystal optical element according to Claim 1, 2, 3, 4 or 5, wherein the mixture contains a very small amount of a curing catalyst.

25 **【Claim 7】**

The method for producing a liquid crystal optical element according to any one of Claims 1 to 6, wherein

the mixture contains a chiral agent.

【Claim 8】

The method for producing a liquid crystal optical element according to any one of Claims 1 to 7, wherein a
5 plurality of compounds of the formula (1) wherein n and m are different, are used in combination.

【Claim 9】

A liquid crystal optical element produced by the method as defined in any one of Claims 1 to 8.

10 **【DETAILED DESCRIPTION OF THE INVENTION】**

【Technical Field to which the Invention Belongs】

The present invention relates to a liquid crystal optical element whereby the transmittance, scattering and reflection state of the element is controlled by
15 application/non-application of an electric field and which is useful for e.g. a light-controlling element, a display element or an optical shutter.

【Prior Art】

A transmission/scattering type optical element has
20 been proposed in which a liquid crystal and a transparent polymer are combined to form a difference in the refractive index between the polymer and the liquid crystal or in the interior of the liquid crystal (among microscopic regions). It is called, for example, a
25 liquid crystal/polymer composite element, a liquid crystal/resin composite element or a dispersion type liquid crystal element. In principle, this element

requires no polarizing plate, whereby the light absorption loss is small, and a high scattering performance can be obtained, and thus, it has a significant merit in that the light-utilizing efficiency
5 in the entire element is high.

By utilizing such characteristics, it is employed for a light-controlling glass, an optical shutter, a laser apparatus and a display apparatus. One showing a scattering state under application of no voltage and a
10 transparent state under application of a voltage, has been commercialized.

Further, prior art reference 1 (USP 5,188,760) discloses an element employing a liquid crystal and a polymerizable liquid crystal. According to this prior
15 art reference 1, under application of no voltage, the element shows a transparent state as observed from any direction as the liquid crystal and the polymerized liquid crystals in the element have the same alignment direction, and under application of a voltage, the
20 alignment of the liquid crystals in the element is controlled by an electric field, and the alignment direction of liquid crystal molecules changes variously in the microscopic regions, whereby the element shows a scattering state.

25 Further, it has been disclosed that the contrast ratio can be improved by adding a chiral agent to provide a helical structure in the initial alignment. This

element is called "an anisotropic gel" or "a liquid crystal gel". In this prior art reference 1, a mesogen monomer having acryloyl groups at the terminals was used.

Further, prior art reference 2 (PCT International Publication WO92/19695) also discloses an element having a similar structure. The operation mode was the same as in prior art reference 1, and a very small amount of a polymer is dispersed in the chiral nematic liquid crystal to obtain a transparent state under application of no voltage and a scattering state under application of a voltage. This element is called PSCT (polymer stabilized cholesteric texture). Also in this prior art reference 2, a mesogen monomer having acryloyl groups at the terminals, was disclosed.

15 **【Problems that the Invention is to Solve】**

Characteristics of a liquid crystal optical device obtained by preparing a mixture comprising a liquid crystal and an uncured curable compound, and curing the curable compound to form a liquid crystal/cured composite layer, depend largely on the structure of the liquid crystal/cured composite. Further, the molecular structure of the uncured curable compound to be used, will give a substantial influence over the structure of the formed liquid crystal/cured composite.

25 It has been reported that in general, with a curable compound containing a mesogen structure such as a biphenyl structure, curable sites at both ends will bond,

the modulus of elasticity after being cured is large, and the glass transition temperature of the obtainable polymer is also high.

On the other hand, this means that restrictions are given to the free volume and the molecular motion of the curable compound during the curing, and at the later stage of the curing process, the reactivity of the curable sites is likely to be suppressed, and there has been a problem that the curing reaction tends to be not enough, or a very long curing time will be required.

Further, with the liquid crystal optical elements of the prior art references, the voltage transmittance curves of the elements were likely to change by driving of application of an electric field for a plurality of times, and the contrast between application and non-application of an electric field, was still low.

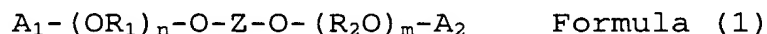
The present invention provides a liquid crystal optical element having high reliability and high contrast, whereby the voltage transmittance curve of the element will not substantially change even by driving of application or non-application of an electric field for a plurality of times. Further, it provides a production method whereby a liquid crystal optical element can be produced easily and constantly in good yield.

25 **【Means of Solving the Problems】**

The first embodiment of present invention provides a method for producing a liquid crystal optical element,

which comprises sandwiching a mixture of a liquid crystal with an uncured curable compound between a pair of substrates which are provided with transparent electrodes and of which at least one is transparent, and curing the curable compound to form a liquid crystal/cured composite layer, wherein the curable compound contains a compound of the formula (1):

5 **[Ka 2]**



10 wherein each of A_1 and A_2 which are independent of each other, is an acryloyl group, a methacryloyl group, a glycidyl group or an allyl group; each of R_1 and R_2 which are independent of each other, is a C_{2-6} alkylene group; Z is a bivalent mesogen structure; and each of n and m which are independent of each other, is an integer of from 1 to 10.

Further, the second embodiment of the present invention provides the above-mentioned method wherein Z is a 4,4'-biphenylene group, or a 4,4'-biphenylene group having part or all of hydrogen substituted by C_{1-2} alkyl or halogen atoms.

Further, the third embodiment of the present invention provides the production method wherein each of R_1 and R_2 which are independent of each other, is an ethylene group or a propylene group.

Further, the fourth embodiment of the present invention provides the production method wherein each of

A₁ and A₂ which are independent of each other, is an acryloyl group or a methacryloyl group.

Further, the fifth embodiment of the present invention provides the production method wherein each of
5 n and m which are independent of each other, is from 1 to 4.

Further, the sixth embodiment of the present invention provides the production method wherein the mixture contains a very small amount of a curing agent.

10 Further, the seventh embodiment of the present invention provides the production method wherein the mixture contains a chiral agent.

Further, the eighth embodiment of the present invention provides the production method wherein a
15 plurality of compounds of the formula (1) wherein n and m are different, are used in combination.

Further, the ninth embodiment of the present invention provides a liquid crystal optical element produced by means of the above production method.

20 **【Mode of Carrying out the Invention】**

In the present invention, an oxyalkylene structure having a high molecular mobility is introduced between the mesogen structural portion and the curable site in the uncured curable compound, whereby the molecular
25 mobility at the curable site in the curing process can be improved, and it is possible to obtain a liquid crystal optical element which has a high reliability and a high

contrast, even by a curing reaction for a short time, whereby the state under application or non-application of an electric field, is stable. In Figure 1, a flow chart of one embodiment of the method for producing a liquid
5 crystal optical element of the present invention, will be shown.

The curable sites (A_1 , A_2) of the formula (1) may be any of the above-mentioned functional groups which are photo curable or heat curable usually in the presence of
10 a curing catalyst. Among them, an acryloyl group or a methacryloyl group suitable for photo curing, is preferred, since the temperature for the curing can be controlled.

The carbon numbers of the oxyalkylene portions R_1 and
15 R_2 of the formula (1) are preferably from 2 to 6 from the viewpoint of the mobility. Further, a chain of an ethylene group having a carbon number of 2 and a propylene group having a carbon number of 3, are preferred.

20 As the mesogen structural portion (Z) of the formula (1), a bivalent polyphenylene having at least two 1,4-phenylene groups bonded, is preferred. Further, some of 1,4-phenylene groups in this polyphenylene group may be bivalent organic groups substituted by a 1,4-
25 cyclohexylene group.

Some or all of the hydrogen atoms of such a polyphenylene group or a bivalent organic group may be

substituted by a substituent such as a C_{1-2} alkyl group, a halogen atom, a carboxyl group or an alkoxycarbonyl group. Preferred Z is a biphenylene group having two 1,4-phenylene groups bonded (hereinafter referred to as a 4,4'-biphenylene group), a terphenylene group having three such phenylene groups bonded, and a bivalent organic group having from 1 to 4 hydrogen atoms of such a group substituted by a C_{1-2} alkyl group, a fluorine atom, a chlorine atom or a carboxyl group. Most preferred Z is a 4,4'-biphenylene group having no substituent.

If n and m of the formula (1) are too large, the compatibility with the liquid crystal deteriorates, and each of them is from 1 to 10, further preferably from 1 to 4 taking into consideration the characteristics of the element after curing.

The mixture of a liquid crystal with an uncured curable compound, may contain a curing catalyst, and in the case of photo curing, a photo polymerization initiator which is commonly used for a photo curable resin may be employed such as a benzoin ether type, an acetophenone type or a phosphine oxide type.

In the case of thermosetting, a curing catalyst such as a peroxide type, a thiol type, an amine type or an acid anhydride type, may be used depending upon the type of the curable sites, and if necessary, a curing assistant such as an amine may also be used.

The content of the curing catalyst is preferably at

most 20 wt% of the uncured curable compound contained, and in a case where a high molecular weight or a high resistivity is required for the cured product after curing, it is more preferably from 1 to 10 wt%.

5 Further, in order to improve the contrast of the element between application and non-application of an electric field, a chiral agent may be added to the mixture of a liquid crystal with an uncured curable compound.

10 In order to improve the compatibility with liquid crystal, the uncured curable compound in the mixture of liquid crystal with the curable compound, may contain a plurality of uncured curable compound differing in n and m in the formula (1), whereby the contrast may further be
15 improved.

On the other hand, the mixture of a liquid crystal with an uncured curable compound, is preferably a homogeneous solution after mixing. Further, the mixture of a liquid crystal with an uncured curable compound may
20 show a liquid crystal phase when sandwiched between the substrates provided with electrodes.

The mixture of a liquid crystal with an uncured curable compound, may show a liquid crystal phase when it is cured. It is also possible to impart a function to
25 align the liquid crystal to the electrode surface by directly abrading the electrode surface of the substrates provided with electrodes, which sandwich the mixture of a

liquid crystal with an uncured curable compound, or by forming a thin film of a resin thereof and rubbing the thin film, whereby it is possible to reduce irregularities at the time of sandwiching the mixture of
5 a liquid crystal and an uncured curable compound.

Further, the combination of the alignment directions of the pair of alignment-treated substrates may be parallel or orthogonal, and the angle may be set to make the irregularities be minimum at the time of sandwiching
10 the mixture.

The distance between the electrodes may be maintained by e.g. a spacer, and the gap is preferably from 4 to 50 μm , more preferably from 5 to 30 μm . If the electrode gap is too small, the contrast tends to
15 deteriorate, and if it is too large, the driving voltage will increase. Figure 2 shows a schematic cross-sectional view of a liquid crystal optical element of the present invention.

It is a liquid crystal optical element 10 comprising
20 glass substrates 1A and 1B, electrodes 2A and 2B, alignment films 3A and 3B and a liquid crystal/cured composite layer 4. It is an element which exhibits a transparent state at the time of non-application of a voltage and a scattering state at the time of application
25 of a voltage. Figure 3 is a view schematically illustrating a state in which a liquid crystal optical element of the present invention is used as a window

glass of an automobile. It has a merit in that the transmittance in an oblique direction is high.

The substrates supporting electrodes, may be glass substrates or resin substrates, or a combination of a glass substrate and a resin substrate. Further, one side may be a reflecting electrode made of an aluminum or dielectric multi-layer film.

In the case of film substrates, the productivity is high, because it is possible that continuously supplied substrates provided with electrodes, are sandwiched between pairs of rubber rolls, and a mixture of a liquid crystal and an uncured curable compound, having a spacer incorporated and dispersed therein, is sandwiched between them, followed by continuous curing.

In the case of glass substrates, a very small amount of a spacer is distributed inside of the electrode surfaces, and the four sides of the opposing substrates are sealed with a sealing agent such as an epoxy resin to form a sealed cell, and one of cutouts of the seal formed at two or more portions is dipped in a mixture of a liquid crystal with an uncured curable compound, and suctioning from the other to fill the mixture into the cell, followed by curing to obtain a liquid crystal optical element. Otherwise, a vacuum injection method may also be employed.

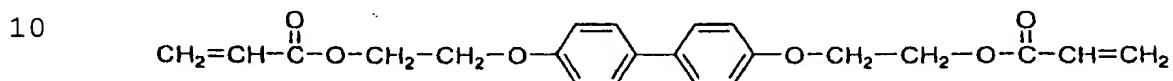
Now, the present invention will be described in detail with reference to Examples 1 to 7 (Examples of the

present invention) and Examples A to E (Comparative Examples).

EXAMPLE 1

A mixture (mixture A) comprising 95 parts of a cyano
5 type nematic liquid crystal (BL-006, manufactured by Merck, dielectric anisotropy: positive), 5 parts of an uncured curable compound of the formula (2) and 0.15 part of benzoin isopropyl ether, was prepared.

【Ka 3】



Formula (2)

This compound of the formula (2) corresponds to a compound of the formula (1) wherein A_1 and A_2 are each an
15 acryloyl group, R_1 and R_2 are each an ethylene group, the mesogen structural portion of Z is a 4,4'-biphenylene group, and each of n and m is 1.

This mixture A was injected into a liquid crystal cell prepared by disposing a pair of substrates having
20 polyimide thin films formed on transparent electrodes and rubbed in one direction, to face so that the rubbing directions crossed each other, dispersing a very small amount of resin beads having a diameter of 13 μm , and bonding the substrates via the resin beads by an epoxy
25 resin printed along the four sides with a width of about 1 mm.

This liquid crystal cell was maintained at 25°C and

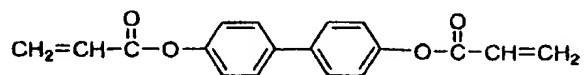
ultraviolet rays of 3 mW/cm² from the upper side and
ultraviolet rays of about 3 mW/cm² from the lower side,
were irradiated for 10 minutes by a HgXe lamp having a
main wavelength of about 365 nm, to prepare a liquid
5 crystal optical element.

An operation of applying a voltage of 50 Vrms with a
rectangular wave of 50 Hz to this liquid crystal optical
element for 10 minutes and then removing the voltage, was
repeated ten times. Then, the transmittance of the
10 liquid crystal cell was measured by a transmittance
measuring system (F value of the optical system: 11.5)
employing a measuring light source having a center
wavelength of 530 nm and a full width at half maximum
value of about 20 nm, whereby the transmittance was 79%
15 in a state where no voltage was applied, 23% in a state
where 50 Vrms was applied, and the difference in the
transmittance between application and non-application of
the voltage, was 56%.

EXAMPLE A

20 A liquid crystal optical element was prepared in the
same manner as in Example 1 except that an uncured
curable compound of the formula (3) (4,4'-
bisacryloyloxybiphenyl) was used instead of the compound
of the formula (2) as the uncured curable compound.

25 **[Ka 4]**



Formula (3)

This compound of the formula (3) corresponds to a compound of the formula (1) wherein A_1 and A_2 are each an acryloyl group, the mesogen structural portion of Z is a 4,4'-biphenylene group, and each of n and m is 0.

5 To this liquid crystal optical element, a voltage was applied in the same manner as in Example 1. Then, the transmittance was measured by the same measuring system as in Example 1, whereby the transmittance was 72% in a state where no voltage was applied, 29% in a state
10 where 50 Vrms was applied, and the difference in the transmittance between the application and non-application of the voltage, was 43%.

EXAMPLE 2

A mixture (mixture B) having 2.5 wt% of a chiral
15 agent (a mixture of S-811, manufactured by Merck and C15 manufactured by Merck in a weight ratio of 1:1) dissolved in mixture A prepared in Example 1, was prepared.

This mixture B was injected into the same liquid crystal cell as in Example 1, and while maintaining it at
20 25°C, ultraviolet rays of 3 mW/cm² from the upper side and ultraviolet rays of about 3 mW/cm² from the lower side were irradiated for 3 minutes by the same HgXe lamp having a main wavelength of about 365 nm as in Example 1, to obtain a liquid crystal optical element.

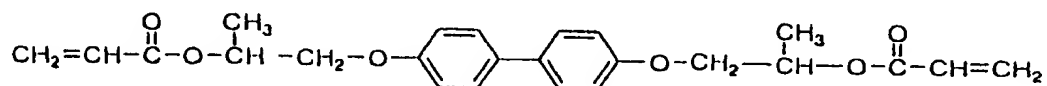
25 An operation of applying a voltage of 50 Vrms with a rectangular wave of 50 Hz to this liquid crystal optical element for 10 minutes and then removing the voltage, was

repeated ten times. Then, the transmittance was measured by a transmittance measuring system (F value of the optical system: 11.5) employing a measuring light source having a center wavelength of 530 nm and a full width at half maximum value of about 20 nm, whereby the transmittance was 78% in a state where no voltage was applied, and the value of a contrast obtained by dividing this value by the transmittance at the time when 50 Vrms was applied, was 33.

10 EXAMPLE 3

A liquid crystal optical element was obtained in the same manner as in Example 2 except that an uncured curable compound of the formula (4) was used instead of the compound of the formula (2) as the uncured curable compound.

[Ka 5]



Formula (4)

20 This compound of the formula (4) corresponds to a compound of the formula (1) wherein A_1 and A_2 are each an acryloyl group, R_1 and R_2 are each a propylene group, the mesogen structural portion of Z is a 4,4'-biphenylene group, and each of n and m is 1.

25 To this liquid crystal optical element, a voltage was applied in the same manner as in Example 2, and then the transmittance was measured by the same measuring

system, whereby the transmittance was 80% in a state where no voltage was applied, and the value of a contrast obtained by dividing this value by the transmittance at the time when 50 Vrms was applied, was 28.

5 EXAMPLE B

A liquid crystal optical element was obtained in the same manner as in Example 2 except that a compound of the formula (3) was used instead of the compound of the formula (2) as the uncured curable compound. To this
10 liquid crystal optical element, a voltage was applied in the same manner as in Example 2, and then the transmittance was measured by the same measuring system whereby the transmittance was 61% in a state where no voltage was applied, and the value of a contrast obtained
15 by dividing this value by the transmittance at the time when 50 Vrms was applied, was 17.

EXAMPLE 4

A mixture (mixture C) comprising 97 parts of one having 2.5 wt% of the chiral agent used in Example 2,
20 uniformly dissolved in a cyano type nematic liquid crystal (BL-009, manufactured by Merck), 3 parts of an uncured curable compound of the formula (2) and 0.09 part of benzoin isopropyl ether, was prepared.

This mixture C was injected into the same liquid
25 crystal cell as in Example 1, and while maintaining at 25°C, ultraviolet rays of 3 mW/cm² from the upper side and ultraviolet rays of about 3 mW/cm² from the lower

side, were irradiated for 30 minutes by the same HgXe lamp having a main wavelength of about 365 nm as in Example 1, to obtain a liquid crystal optical element.

An operation of applying a voltage of 20 Vrms with a rectangular wave of 50 Hz to this liquid crystal optical element for 10 minutes and then removing the voltage, was repeated ten times. Then, the transmittance was measured by the same transmittance measuring system as mentioned above employing a measuring light source having a center wavelength of 530 nm and a full width at half maximum value of about 20 nm, whereby the transmittance was 82% in a state where no voltage was applied, and the value of a contrast obtained by dividing this value by the transmittance at the time when 20 Vrms was applied, was 11.

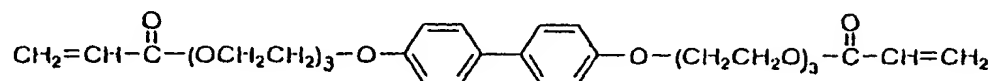
Further, an operation of applying a voltage of 30 Vrms with a rectangular wave of 50 Hz to this liquid crystal optical element for 10 minutes and then removing the voltage, was repeated ten times, and then the transmittance was measured in the same manner, whereby the transmittance was 82% in a state where no voltage was applied, and the value of a contrast obtained by dividing this value by the transmittance at the time when 30 Vrms was applied, was 40.

25 EXAMPLE 5

A mixture (mixture D) comprising 97 parts of one having 2.5 wt% of the chiral agent used in Example 2,

uniformly dissolved in a cyano type nematic liquid crystal (BL-009, manufactured by Merck), 2 parts of an uncured curable compound of the formula (2), 1 part of an uncured curable compound of the formula (5) and 0.09 part of benzoin isopropyl ether, was prepared.

【Ka 6】



Formula (5)

This compound of the formula (5) corresponds to a compound of the formula (1) wherein A_1 and A_2 are each an acryloyl group, R_1 and R_2 are each an ethylene group, the mesogen structural portion of Z is a 4,4'-biphenylene group, n is 2, and m is 3.

This mixture D was injected into the same liquid crystal cell as in Example 1, and while maintaining it at 25°C, ultraviolet rays of 3 mW/cm² from the upper side and ultraviolet rays of about 3 mW/cm² from the lower side, were irradiated for 30 minutes by the same HgXe lamp having the main wavelength of about 365 nm as in Example 1, to prepare a liquid crystal optical element.

An operation of applying a voltage of 20 Vrms with a rectangular wave of 50 Hz to this liquid crystal optical element for 10 minutes and then removing the voltage, was repeated ten times. Then, the transmittance was measured by the same transmittance measuring system as mentioned above employing a measuring light source having a center

wavelength of 530 nm and a full width at half maximum value of about 20 nm, whereby the transmittance was 82% in a state where no voltage was applied, and the value of a contrast obtained by dividing this value by the
5 transmittance at the time when 20 Vrms was applied, was 28.

COMPARATIVE EXAMPLE C

A liquid crystal optical element was obtained in the same manner as in Example 4 except that a compound of the
10 formula (3) was used instead of the compound of the formula (2) as the uncured curable compound. An operation of applying a voltage of 20 Vrms with a rectangular wave of 50 Hz to this liquid crystal optical element for 10 minutes and then removing the voltage, was
15 repeated ten times.

Then, the transmittance was measured by the same transmittance measuring system as mentioned above employing a measuring light source having a center wavelength of 530 nm and a full width at half maximum
20 value of about 20 nm, whereby the transmittance was 57% in a state where no voltage was applied, and the value of a contrast obtained by dividing this value by the transmittance at the time when 20 Vrms was applied, was 10.

25 Further, an operation of applying a voltage of 30 Vrms with a rectangular wave of 50 Hz to this liquid crystal optical element for 10 minutes and then removing

the voltage, was repeated ten times, and then the transmittance was measured in the same manner as described above, whereby the transmittance was 49% in a state where no voltage was applied, and the value of a contrast obtained by dividing this value by the transmittance at the time when 30 Vrms was applied, was 6.

EXAMPLE 6

A mixture (mixture E) having 65 parts of a cyano type nematic liquid crystal (BL-006, manufactured by Merck), 35 parts of a chiral agent (a mixture of R-811, manufactured by Merck and CB15 manufactured by Merck in a weight ratio of 1:1), 3.1 parts of an uncured curable compound of the formula (2) and 0.09 part of benzoin isopropyl ether, was prepared.

This mixture E was injected into the same liquid crystal cell as in Example 1, and while maintaining it at 25°C, ultraviolet rays of 3 mW/cm² from the upper side and ultraviolet rays of about 3 mW/cm² from the lower side, were irradiated for 30 minutes by the same HgXe lamp having a main wavelength of about 365 nm as in Example 1, to prepare a liquid crystal optical element.

An operation of applying a voltage of 50 Vrms with a rectangular wave of 50 Hz to this liquid crystal optical element for 10 minutes and then removing the voltage, was repeated ten times. Then, the liquid crystal optical element was placed on black paper which did not

substantially reflect light, and the reflectance was measured by a reflectance measuring system (F value of the optical system: 8.2) employing a measuring light source having a center wavelength of 530 nm and a full width at half maximum value of about 20 nm, whereby the reflectance was 23% when no voltage was applied, 8% when 50 Vrms was applied, and the difference in reflectance between application and non-application of the voltage was 15%.

10 EXAMPLE D

A liquid crystal optical element was obtained in the same manner as in Example 6 except that a compound of the formula (3) was used instead of the compound of the formula (2) as the uncured curable compound. To this liquid crystal optical element, the voltage was applied in the same manner as in Example 5, and the reflectance was measured by the same measuring system, whereby the reflectance was 16% when no voltage was applied and 9% when 50 Vrms was applied, and the difference in reflectance between application and non-application of the voltage, was 7%.

EXAMPLE 7

A mixture (mixture F) comprising 95 parts of a nematic liquid crystal having a negative dielectric anisotropy ($T_c=98^{\circ}\text{C}$, $\Delta\epsilon=-5.6$, $\Delta n=0.220$), 5 parts of an uncured curable compound of the formula (2), and 0.15 part of benzoin isopropyl ether, was prepared.

This mixture F was injected into a liquid crystal cell prepared by bonding a pair of substrates having thin polyimide films for vertical alignment formed on transparent electrodes so that the thin polyimide films
5 faced each other, via a very small amount of resin beads of 6 μm , by an epoxy resin printed in a width of about 1 mm along the four sides.

While maintaining this cell at 25°C, ultraviolet rays of 3 mW/cm^2 from the upper side and ultraviolet rays of
10 about 3 mW/cm^2 from the lower side were irradiated for 10 minutes by a HgXe lamp having a main wavelength of about 365 nm, to obtain a liquid crystal optical element.

An operation of applying a voltage of 30 Vrms with a rectangular wave of 50 Hz to this liquid crystal optical
15 element for 10 minutes and then removing the voltage, was repeated ten times.

Then, the transmittance was measured by a transmittance measuring system (F value of the optical system: 11.5) employing a measuring light source having a
20 center wavelength of 530 nm and a full width at half maximum value of about 20 nm, whereby the transmittance was 86% in a state where no voltage was applied and 24% in a state where 50 Vrms was applied, and the difference in the transmittance between application and non-
25 application of the voltage, was 62%.

EXAMPLE E

A liquid crystal optical element was obtained in the

same manner as in Example 7 except that a compound of the formula (3) was used instead of the compound of the formula (2) as the uncured curable compound. To this liquid crystal optical element, the voltage was applied in the same manner as in Example 7, and the transmittance was measured by the same measuring system, whereby the transmittance was 64% when no voltage was applied and 20% when 30 Vrms was applied, and the difference in transmittance between application and non-application of the voltage, was 44%. The results of the respective Examples are summarized and shown in the following Table 1.

[Table 1]

Example	Main materials used	conditions	T ^{-VON}	T ^{-VOFF}	ΔT	CR
1	Formula (2)	After	79%	23%	56%	33
2	Formula (2) + chiral agent		78%	About 2%		28
3	Formula (4) + chiral agent		80%	About 3%		11
4	Formula (2) + chiral agent	20 Vrms	82%	About 7%		40
5	Formula (2) + Formula (5) + chiral agent	30 Vrms	82%	About 2%		28
6	Formula (2) + chiral agent	Reflection type	23%	About 3%	15%	
7	Formula (2) + Δε being negative		86%	24%	62%	
A	Formula (3)		72%	29%	43%	17
B	Formula (3) + chiral agent		61%	About 4%		10
C	Formula (3) + chiral agent	20 Vrms	57%	About 6%		6
D	Formula (3) + chiral agent	30 Vrms	49%	About 8%		
E	Formula (3) + Δε being negative	Reflection type	16%	9%	7%	
			64%	20%	44%	
Note	CR represents the contrast ratio, and ΔT represents the differences between T ^{-VON} and T ^{-VOFF} .					

The liquid crystal optical element of the present invention has high transmittance when it is transparent and has a high contrast or difference in transmittance between application and non-application of an electric field, and thus is suitable for e.g. an optical shutter or a light-controlling glass which is required to provide a high light transmittance when it is transparent.

Also when made into a reflection type liquid crystal optical element, it has a high reflectance at the time when no voltage is applied, and the contrast between application and non-application of an electric field can be made high.

Further, the change in the voltage-transmittance curve or the voltage-reflectance curve due to repetition of an operation of application and non-application of an electric field to the liquid crystal optical element, is small, whereby it is possible to present a highly reliable liquid crystal optical element.

【Brief Explanation of the Drawings】

20 **【Figure 1】**

A flow chart showing an embodiment of the method for producing a liquid crystal optical element of the present invention.

【Figure 2】

25 A diagrammatic cross-sectional view of an embodiment of the liquid crystal optical element of the present invention.

【Figure 3】

A diagrammatic view showing an embodiment of use of the liquid crystal optical element of the present invention.

5 **【Explanation of the Reference Numerals】**

1A, 1B: Glass substrates

2A, 2B: Electrodes

3A, 3B: Alignment films

4: Liquid crystal/cured composite layer

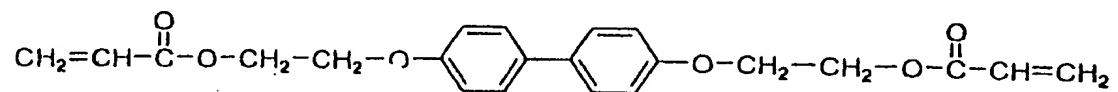
10 10: Liquid crystal optical element

【TYPE OF DOCUMENT】

DRAWING

【Fig. 1】

A MIXTURE OF A COMPOUND OF THE FORMULA:



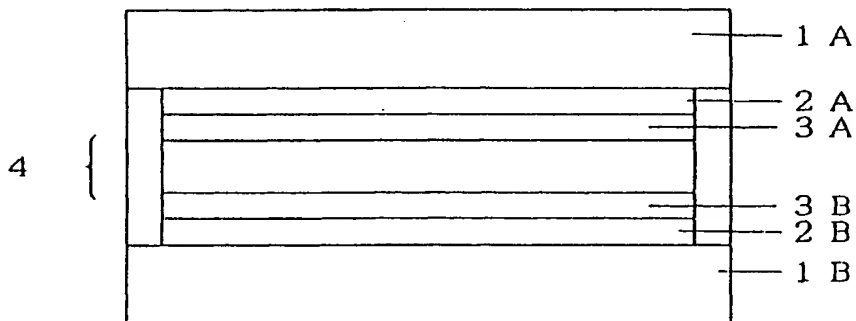
WITH A LIQUID CRYSTAL, IS SANDWICHED BETWEEN A PAIR OF SUBSTRATES PROVIDED WITH ELECTRODES



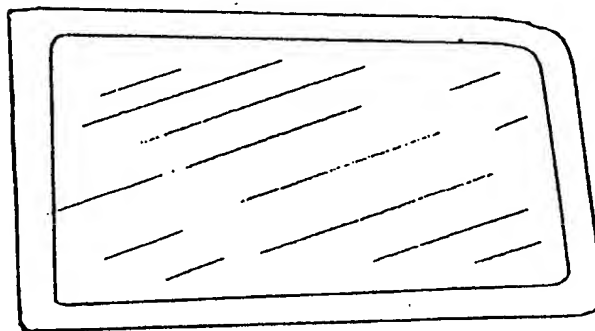
THE CURABLE COMPOUND IS CURED

【Fig. 2】

$\frac{10}{\sim}$



【Fig. 3】



【TYPE OF DOCUMENT】 ABSTRACT

【SUMMARY】

【OBJECT】

It is an object to obtain an element which has
5 excellent optical characteristics and undergoes small
change in characteristics even if repeatedly used.

【MEANS OF SOLVING PROBLEMS】

A liquid crystal/cured composite layer is formed by
sandwiching a mixture of a liquid crystal with an uncured
10 curable compound i.e. a curable compound represented by a
structure of an acryloyl group- $(OR_1)_n$ -O-mesogen
structural portion-O- $(R_2O)_m$ -acryloyl group structure
(wherein each of R_1 and R_2 is a C_{2-6} alkylene group, and
each of n and m is from 1 to 10), between a pair of
15 substrates provided with transparent electrodes, and
curing the curable compound.

【SELECTED FIGURE】 Figure 1